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ENERGY LEVELS IN AND ON AN OXIDE FILM AS MEASURED BY ELECTROCHE--ETC(U)  
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For the Period 14 Jul 1978 - 14 Aug 1981

ENERGY LEVELS IN AND ON AN OXIDE FILM AS  
MEASURED BY ELECTROCHEMICAL METHODS

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FINAL REPORT

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  - a. Electron Exchange at the Surface of Thermally Grown Silica, M. J. Madou, K. W. Frese, Jr., and S. R. Morrison, J. Electrochemical Soc. 126, 827 (1979).
  - b. The Si/SiO<sub>2</sub> Electrode, S. R. Morrison, M. J. Madou, and K. W. Frese, Jr., Phys. Stat. Sol. A57, 705 (1980).
  - c. Imperfections In and Ion Diffusion Through Oxide Layers on Silicon, S. R. Morrison, M. J. Madou, and K. W. Frese, Jr., Appl. Surf. Sci. 6, 138 (1980).
  - d. Bulk and Surface Characterization of the Silicon Electrode, M. J. Madou, B. H. Loo, K. W. Frese, Jr., and S. R. Morrison, Surface Sci. 108, 135 (1981).
  - e. The Introduction of Impurities in Anodically Grown Silica, M. J. Madou and S. R. Morrison, submitted to J. Electrochem. Soc.
  - f. Ultraviolet Bleaching and Regeneration of Si = Si<sub>3</sub> Centers at the Si/SiO<sub>2</sub> Interface of Thinly Oxidized Silicon Wafers, E. H. Poindexter, P. J. Caplan, and S. R. Morrison, in preparation.
  - g. Electrochemistry at Semiconductor and Oxidized Metal Electrodes, S. R. Morrison (Plenum Press, New York, 1980). (Much of the discussion in this book of the behavior of oxidized electrodes was based on work done on the Si/SiO<sub>2</sub> electrode under this contract.)

## Review of ARO Program

### ENERGY LEVELS IN AND ON AN OXIDE FILM AS MEASURED BY ELECTROCHEMICAL METHODS

During the three years covered by this report, studies were made of the oxide layer over silicon, using electrochemical methods (supplemented at times by MOS measurements).

The most important conclusion, an early conclusion that provided the key to interpreting many subsequent observations, was that alkali ions diffuse readily into  $\text{SiO}_2$  from solution. Specifically, under a cathodic bias, alkali metals from solution (and perhaps hydrogen) can diffuse at room temperature through a thick (up to 4000 Å) oxide layer, building up in concentration at the  $\text{Si}/\text{SiO}_2$  interface. When the concentration of alkali ions becomes sufficiently high, a space charge induced narrow barrier appears at the interface, permitting tunneling of carriers between the silicon and otherwise inaccessible levels in the  $\text{SiO}_2$ .

With this model, many features are explainable. For example, it is easily understood why, under a separate cathodic bias, the  $\text{SiO}_2$  layer becomes conductive, but under zero or anodic bias the conductivity quickly disappears (the positive ions move away from the interface). Again from an analysis of the bias needed (found to be greater than -2 V SCE), it was concluded that the 2.4 eV levels in the  $\text{SiO}_2$  provide the conducting impurity band--a conclusion consistent with others' observations that a positively charged species provides the ubiquitous 2.4 eV level. With such impurity band conductance, it is reasonable that the  $\text{SiO}_2$  shows a metallic behavior as an electrode--the electrode potential for current flow matches the redox potential of the species in solution. Finally the model of diffusion of the sodium into the  $\text{SiO}_2$  describes accurately the relation between the oxide thickness and the time under cathodic bias necessary to induce the conductance. A mobility for sodium ions of  $2 \times 10^{-14} \text{ cm}^2/\text{V sec}$  is determined.

The observations and model, incidentally, provide a simple explanation of why in general valve metal oxides, that are so insulating under anodic bias, are always found to break down rapidly under cathodic bias. Silicon is a classic "valve metal" (like tantalum, aluminum) except that it is actually a semiconductor, allowing more versatility in the experimentation. Alkali or proton diffusion through the oxide, followed by F/N tunneling would be expected to be common for valve metal oxides, explaining the asymmetric behavior.

With the behavior of  $\text{SiO}_2$  with additives reasonably understood, the emphasis was shifted to a problem of great interest to the Army, oxide breakdown. It was found, simply by observing the hydrogen generation under cathodic bias, that the conductance through the  $\text{SiO}_2$  was highly non-uniform. Because of the interest of the Army in thin oxide layers for MOS devices that are breakdown resistant, we studied further the origin of the flaws leading to the easily observable (electrochemically) current flow. It was found that some impurities, particularly Group II, would cause the breakdown, and mechanical damage to the surface of the  $\text{SiO}_2$  would lead to breakdown. It was suggested that in both cases the basic origin is the crystallization of the local region of the oxide, with the crystallization induced by the impurity or initiated by the surface damage.

As the glass-forming tendency of silica is very sensitive to various kinds of impurity, we began a study with various impurities to determine whether impurities could be introduced that resisted the crystallization. Such studies have been pursued in the last part of the present contract and were planned for a continuing study.

In the first phase of this study of impurities, done under the present contract, ions were studied that can be introduced into the silica electrochemically. Specifically we studied phosphorus and sulfur introduced in the form of phosphate or sulfate groups.

The ions were found to be highly mobile at room temperature, but with an annealing treatment above about  $500^\circ\text{C}$  the ions become immobile and reverse their charge from negative to positive. However, most of

the ions evaporate from the oxide during the annealing. In the last months of the contract, studies were under way where the ions were introduced at room temperature, forced by an electric field to the interface, and, with the field still applied to hold the ions in, the oxide was heated to immobilize the ions. Only temperatures up to 100° were examined in the time available, but positive results were obtained--a substantial flatband shift was observed at room temperature depending on whether the sample had been held anodic or cathodic during the high temperature annealing.

#### RECOMMENDATIONS

A continuation of these studies of the introduction of charge compensated immobile ions into the oxide and of their influence on the electrical breakdown of the oxide, may be beneficial both from a basic and an applied viewpoint. The results may provide an approach to the use of much thinner oxides and thus much closer component packing of MOS devices in VLSI.

